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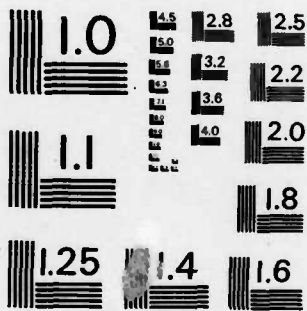
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roscopic and electrochemical data indicate that these compounds are stable in the neutral (1:1) and acid (mole ratio >1) melts, while $\text{Ru}(\text{bpy})_3^{2+}$ is stable in basic melts (mole ratio <1), but $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ decompose to FeCl_4^{2-} . Comparison of the formal potentials for M(III)/(II) -polypyridine couples studied here and in other solvents indicate that the redox properties of these complexes are relatively insensitive to the nature of the solvent. It was shown that oxygen acts as an oxidant in the acid melts to oxidize $\text{Fe}(\text{bpy})_3^{2+}$, $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ to their corresponding $3+$ form. The $3+$ form of each complex was stable in acid melts for several weeks. Perchlorate is also shown to function as an oxidant in acidic melts.

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TECHNICAL REPORT NO. 18

ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES OF POLYPYRIDINE COMPLEXES
OF Fe(II)/(III) and Ru(II)/(III) IN THE
ALUMINUM CHLORIDE: N-(1-Butyl)PYRIDINIUM CHLORIDE MOLTEN SALT

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ABSTRACT

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The electrochemical and spectroscopic behavior of $\text{Fe}(\text{bpy})_3^{2+}$, $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ in an ambient-temperature molten salt system, aluminum chloride:N-(1-butyl)pyridinium chloride (BuPyCl) have been studied as a function of melt composition. The complexes show a single one-electron reversible oxidation wave from melt compositions of 1:1 to 2:1 (AlCl_3 :BuPyCl mole ratio). Visible spectroscopic and electrochemical data indicate that these compounds are stable in the neutral (1:1) and acid (mole ratio >1) melts, while $\text{Ru}(\text{bpy})_3^{2+}$ is stable in basic melts (mole ratio <1), but $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ decompose to FeCl_4^{2-} .

Comparison of the formal potentials for M(III)/(II)-polypyridine couples studied here and in other solvents indicate that the redox properties of these complexes are relatively insensitive to the nature of the solvent. It was shown that oxygen acts as an oxidant in the acid melts to oxidize $\text{Fe}(\text{bpy})_3^{2+}$, $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ to their corresponding 3+ form. The 3+ form of each complex was stable in acid melts for several weeks.

Perchlorate is also shown to function as an oxidant in acidic melts.

INTRODUCTION

The molten salt system composed of aluminum chloride and N-(1-butyl)pyridinium chloride (BuPyCl) is liquid at ambient temperatures ($\sim 30^\circ\text{C}$) over a wide compositional range varying from $\sim 0.7:1$ to $2:1$ (mole ratio of AlCl_3 to BuPyCl) (1,2). The Lewis acid-base properties of these melts change as the mole ratio of AlCl_3 to BuPyCl changes. The melts can be characterized as acidic, basic or neutral depending on the mole ratio of AlCl_3 to BuPyCl being greater than, less than or equal to unity (3). In the acidic melts, anionic species are Al_2Cl_7^- and AlCl_4^- , in basic melts AlCl_4^- and Cl^- , and in neutral, AlCl_4^- . It has been shown that equilibrium (1) with the $\log K = -16.9 \pm 2$ (4) provides



an adequate description of the system throughout the entire range of melt composition (2).

In view of their non-lability and extreme stability in the absence of direct illumination, low spin complexes of $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ (where bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline) were chosen to study in $\text{AlCl}_3\text{:BuPyCl}$ melts. These complexes were selected for several reasons. Initially we were interested to know whether these compounds are stable in this molten salt media, i.e. whether the reactant's coordination sphere remains intact while the Lewis acid-base properties of the melts are varied. A second aspect of this work was the examination of the possible use of these complexes as internal reference couples. In addition, the use of these melts as solvents for modified electrode studies, which includes Ru(II)/Ru(III) polymers, suggested such studies (5).

Spontaneous oxidation of hydrocarbons in highly acidic $\text{AlCl}_3\text{:BuPyCl}$ melts has been observed by Robinson and Osteryoung (1). The slow chemical oxidation of iodide in acidic $\text{AlCl}_3\text{:BuPyCl}$ melts has been suggested to be due to a reaction with traces of impurity present in the dry box atmosphere, probably molecular oxygen (6). To determine the true nature of the oxidizing species in the melt, these polypyridine complexes proved to be useful.

The electrochemistry of these transition-metal complexes has been studied both in protic and aprotic solvents (7-17). The oxidation states frequently observed for these complexes are 2+ and 3+. Polypyridine complexes of Ru and Fe with total charges of 1+, 0, and 1- have been observed in solvents with very negative potential windows such as acetonitrile (7,9) and N,N-dimethylformamide (8). Recently more highly oxidized species such as $\text{Ru}(\text{bpy})_3^{4+}$, $\text{Fe}(\text{bpy})_3^{4+}$ and $\text{Fe}(\text{bpy})_3^{5+}$ have been reported in liquid sulfur dioxide (13). We report here electrochemical and spectroscopic investigations of $\text{Fe}(\text{bpy})_3^{2+/3+}$, $\text{Fe}(\text{phen})_3^{2+/3+}$ and $\text{Ru}(\text{bpy})_3^{2+/3+}$ in ambient temperature $\text{AlCl}_3\text{:BuPyCl}$ ionic liquids.

EXPERIMENTAL SECTION

Preparation of N-(1-butyl)pyridinium chloride and purification of aluminum chloride have been described elsewhere (1). $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$ and $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ (G. F. Smith Chemical Co.), FeCl_2 (Alfa Products), FeCl_3 (Fisher), 2,2'-bipyridine (Baker) and 1,10-phenanthroline were used without further purification. Tetraethylammonium perchlorate (TEAP), (Baker) was dried in a vacuum oven and used for experiments testing the ability of perchlorate to function as an oxidant. Aluminum wire (Alfa Products) was cleaned in a 30:30:40 volume mixture of $\text{H}_2\text{SO}_4:\text{HNO}_3:\text{H}_3\text{PO}_4$, rinsed with water and dried. Chemicals were stored and all electrochemical experiments performed under argon atmosphere in a Vacuum Atmospheres Co. dry box.

A Metrohm glass cell covered with a teflon lid which had several holes for reference and counter electrode compartments, working electrode and thermometer was used for the electrochemical measurements. The entire cell assembly was placed in a furnace and the temperature controlled at $40 \pm 1^\circ\text{C}$ by a Thermo Electric Selector 800 temperature controller. Reference and counter electrode compartments were aluminum wires dipped into the 2:1 $\text{AlCl}_3:\text{BuPyCl}$ melt and both were separated from the working compartment by fine glass frits. A glassy carbon disc (GC) electrode obtained from Pine Instrument Co. was used as the working electrode. The GC (with the area of 0.196 cm^2 or 0.454 cm^2) was polished with successively finer grades of 1.0, 0.3 and 0.05 micron alumina (Buehler), then rinsed with water and air dried prior to transfer to the dry box.

All voltammograms were obtained using a EG&G PARC 175 Universal Programmer with a PARC 173 potentiostat and a Houston Omnigraph Model

2000 recorder. A Pine Instrument Co. electrode rotator (Model ASR2) was used for rotating disc electrode (RDE) studies.

UV and visible absorption spectra were recorded in either 0.1 or 1.0 cm path length quartz cells fitted with air-tight Teflon caps using a Perkin Elmer (Coleman 575) spectrophotometer. The cells were filled and sealed in the dry box.

RESULTS

1. ELECTROCHEMISTRY

a. OXIDATION OF $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$:

$\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$ and $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ both dissolve in the neutral (mole ratio = 1.0) and acid (mole ratio >1) melts and give intense red-colored solutions. The solubility of $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ is less than that of $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$, especially in the neutral melt. In Figure 1, typical cyclic voltammograms at a GC electrode are shown for $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$, respectively. Cyclic and rotating disc electrode voltammograms for oxidation of polypyridine complexes of iron(II) were recorded as a function of melt acidity. Tabulations of cyclic and RDE voltammetric parameters, anodic to cathodic peak current ratios i_p^a/i_p^c , the difference between the anodic and cathodic peak potentials $\Delta E_p = E_p^a - E_p^c$, and $i_p^a/\nu^{1/2}$ for $\text{Fe}(\text{bpy})_3^{2+/3+}$ and $\text{Fe}(\text{phen})_3^{2+/3+}$ are presented in Tables 1 and 2, respectively. As shown in Figure 2 plots of the current vs. the square root of the electrode rotation rate at potentials on the rising portion of the waves and on the plateaus for oxidation of both complexes in the neutral melt were linear and passed through the origin, indicating that the oxidation is reversibly convective diffusion-controlled (18). Plots of E vs. $\log \frac{I_k - I}{I}$, constructed from RDE data for oxidation of both polypyridine complexes of Fe(II) were linear with slopes of 65 ± 1 mV ($2.3 \text{ RT/F} = 62$ mV at 40°C) (see Figure 3). Solutions of $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ in the neutral melt were found to be stable for a period of over a week. There was no change in the color of the solutions or their visible spectra. RDE voltammograms were recorded daily for polypyridine complexes

of Fe(II) in the neutral melt. The values of $E_{1/2}$ and anodic limiting current, I_1^a , were found to be constant within experimental error for at least seven days. When a neutral melt containing either of the polypyridine complexes of iron was made acidic by addition of $AlCl_3$, RDE voltammograms showed both cathodic and anodic current, indicating the presence of both the reduced and oxidized form of tris-bpy and tris-phen complexes of iron in the solution. Indeed in the 1.05:1 melt the cathodic limiting current, I_1^c , is <5% of the total limiting current, $I_1^t = I_1^c + I_1^a$. As the acidity of the melt increased the I_1^c/I_1^a ratio also increased and the color of the solution changed from red to dark brown and finally to blue. When the melt composition approached 1.9:1 almost all the complex was in the oxidized form. This oxidation of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ not only occurred with increased melt acidity (i.e., increase in $AlCl_3$ concentration), but as shown in Figure 4, even when a 1.2:1 melt containing 3.8 mM $Fe(bpy)_3^{2+}$ was kept in the dry box, I_1^c increased with time while I_1^a decreased. After about two hours I_1^c was ~ 3 times larger and I_1^a ~ 3 times smaller than their initial values. Thus, $\sim 75\%$ $Fe(bpy)_3^{2+}$ was oxidized to $Fe(bpy)_3^{3+}$ in less than two hours and eventually almost all of it was oxidized. It has been suggested that the slow chemical oxidation of I^- (with $E_{1/2} \approx 1$ V), in an acidic $AlCl_3$:BuPyCl melt, resulted from a reaction with traces of impurity present in the dry box atmosphere, possibly molecular oxygen (6). Although the dry box atmosphere had an oxygen level of ≤ 5 ppm, it may have been enough to slowly oxidize both $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ complexes to their corresponding 3+ form, although perchlorate can also function as an oxidant (see below). The formation of the oxidized form of these complexes was proved both by RDE

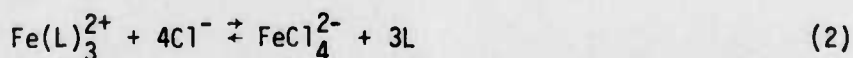
experiments and their visible spectra (see below). Neither the reduction of oxygen nor electrochemistry from its reduction product could be seen directly by the electrochemical techniques. To show that O_2 was an oxidizing species, several other experiments were performed. Acidic $AlCl_3:BuPyCl$ melts with various compositions (1.07:1, 1.2:1 and 1.9:1) were prepared and $Fe(phen)_3(ClO_4)_2$ dissolved in them. These solutions were taken outside the dry box in sealed tubes. When these solutions were purged with oxygen, their color changed from red to blue (although the color change in the less acidic melt, 1.07:1 was slower than in the other melts). The spectra of these solutions were identical to those for acidic solutions of $Fe(phen)_3^{2+}$ which were oxidized slowly to $Fe(phen)_3^{3+}$ in the dry box. These results clearly indicate that oxygen in the acid melts can oxidize $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ to $Fe(bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$, respectively. The rate of the oxidation of these complexes appears to depend both on the amount of oxygen present in the dry box atmosphere and the melt acidity (see below, however). It is obvious from our results that the oxidation of any of these complexes in a given melt by traces of oxygen or perchlorate (see below) does not affect the E_f or $E_{1/2}$ values. The only changes were in the values of I_1^c and I_1^a . In any case the sum of $I_1^c + I_1^a$ (i.e., I_1^t), remained unchanged within experimental error. The oxidized forms of these polypyridine complexes of iron i.e., $Fe(bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$ were stable in acid melts for at least two weeks.

The possibility that perchlorate could function as an oxidant in these systems was examined. As mentioned above, both $Fe(phen)_2^{2+}$ and

$\text{Fe}(\text{bpy})^{2+}$, were added to the melts as perchlorate salts and underwent slow oxidation in the acidic melts, some of which, as demonstrated above, was due to oxygen, but some of which might have been due to the presence of perchlorate. As described below, although the oxidation of the $\text{Ru}(\text{bpy})^{2+}$ complex was observed in very acidic (1.7:1) melts, it appeared much slower than that of the corresponding $\text{Fe}(\text{II})$ complexes. Since the $\text{Ru}(\text{bpy})^{2+}$ salts were chlorides, they were used in experiments to ascertain the effect of perchlorate as an oxidant. If a forty-fold excess of TEAP were added to a 1.7:1 $\text{AlCl}_3:\text{BuPyCl}$ melt containing ca 1 mM $\text{Ru}(\text{bpy})^{2+}$, the orange solution took about 30 minutes to change to green. This compares to much longer periods of time in the absence of perchlorate (see below). In a 1.1:1 melt, visible changes in color took place much more slowly; this was under conditions where, in the absence of perchlorate, no change in the solution color or electrochemistry was noted. In both basic and neutral (i.e., 1.0:1.0) melts, no indication of the oxidation of $\text{Ru}(\text{bpy})^{2+}$ was noted from spectroscopic measurements. These observations indicate that perchlorate, like oxygen, can act as an oxidant only in the acidic melt, that, qualitatively, the oxidation rate increases with increasing melt acidity and that there is no oxidation by perchlorate in the basic or neutral melt. Further experiments on this are in progress (19).

As is the case in other solvents, it was not possible to generate $\text{Fe}(\text{bpy})_3^{3+}$ or $\text{Fe}(\text{phen})_3^{3+}$ simply by adding ligands to an acidic solution of $\text{AlCl}_3:\text{BuPyCl}$ containing FeCl_3 . However, the polypyridine complexes of $\text{Fe}(\text{II})$ were easily obtained in acid melts by mixing FeCl_2 and ligands.

In basic $\text{AlCl}_3\text{:BuPyCl}$ melts (mole ratio <1), it was found that complexes of both $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ decompose and form FeCl_4^{2-} (20). Upon dissolving either of these complexes in the basic melt a red solution was obtained initially which changed within minutes to a light yellow color. Cyclic and RDE voltammograms for $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$ in a 0.95:1 $\text{AlCl}_3\text{:BuPyCl}$ melt are shown in Figure 5. These voltammograms actually correspond to the oxidation of FeCl_4^{2-} to FeCl_4^- . There is excellent agreement between these results and those obtained by Nanjundiah et al., who studied the $\text{FeCl}_4^{2-}/1^-$ couple in basic $\text{AlCl}_3\text{:BuPyCl}$ melts (20). In the "neutral" melt, i.e., mole ratio = 1.0, where the concentration of Cl^- is negligible, both $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ are stable. We found, however, that the addition of even 20 mM BuPyCl (i.e., Cl^-) to a neutral melt containing a 3-4 mM of either of the polypyridine complexes of Fe(II) was sufficient to cause their dissociation to FeCl_4^{2-} . Although Cl^- is a relatively poor nucleophile in aqueous solutions, it seems to be highly reactive toward charged ions in aprotic solvents (21). An investigation of decomposition of tris-phenanthroline Fe(II) in dimethylsulfoxide (DMSO) showed that $\text{Fe}(\text{phen})_3^{2+}$ reacts rapidly with chloride (21,22). The reaction was assumed to be due to anation by chloride, leading to the formation of blue-colored $\text{Fe}(\text{phen})_2\text{Cl}_2$ complex (21). Thus, the complete dissociation of $\text{Fe}(\text{L})_3^{2+}$ (where L = bpy or phen) to FeCl_4^{2-} (see equation 2) in the basic $\text{AlCl}_3\text{:BuPyCl}$ is not surprising.



b. OXIDATION OF $\text{Ru}(\text{bpy})_3^{2+}$:

$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ dissolves throughout the entire range of melt composition giving highly colored orange solutions. The electrochemical oxidation of this complex has been studied by cyclic and rotating disc voltammetry. A typical cyclic voltammogram at a GC electrode is shown in Figure 1. Cyclic and rotating disc electrode voltammograms for oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ were examined as a function of melt composition from 0.8:1 to 2:1. Data obtained from these voltammograms are listed in Table 3. $\text{Ru}(\text{bpy})_3^{2+}$ showed no oxidation or reduction in the basic melt. In acidic or neutral melts only a single oxidation wave was obtained. Table 3 shows scan rate dependencies of peak potentials and peak currents for the $\text{Ru}(\text{bpy})_3^{2+/3+}$ couple. The ratio of one for i_p^a/i_p^c indicates that the electron transfer is reversible over the entire acidic melt composition. For a diffusion-controlled process, $i_p^a/\nu^{1/2}$ should be constant and independent of scan rate; this is true for the present case. Although ΔE_p increases slightly with the scan rate, it does not change with variation in the melt composition. The experimental peak separations (64-70 mV) correspond closely to the theoretical value for a one-electron process of 62 mV at 40°C. Plots of E vs. $\log [I_1 - I/I]$ in all melt compositions studied were linear with slopes of 65 ± 1 mV (see Figure 3).

As with the polypyridine complexes of Fe(II), RDE voltammograms showed that when the acidity of $\text{Ru}(\text{bpy})_3^{2+}$ containing melt increased there was a small cathodic current due to the reduction of $\text{Ru}(\text{bpy})_3^{3+}$

present in the solution. This cathodic current could only be observed when the melt acidity (mole ratio) was greater than $\sim 1.7:1$. Apparently the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ is slower than that of the polypyridine complexes of $\text{Fe}(\text{II})$. The initial I_1^c in a solution of $1.9:1 \text{ AlCl}_3:\text{BuPyCl}$ containing $\text{Ru}(\text{bpy})_3^{2+}$ was about 5% of the I_1^t . Even after two weeks the I_1^c was less than 55% of I_1^t , indicating that $\sim 55\%$ of $\text{Ru}(\text{bpy})_3^{2+}$ was oxidized to $\text{Ru}(\text{bpy})_3^{3+}$. On going from the reduced to the oxidized form of tris-bpy-ruthenium the color of the solution changed from orange to dusty brown and finally to green. As before the nature of the oxidant (i.e., traces of O_2 in the dry box atmosphere) was confirmed by purging acidic solutions of $\text{AlCl}_3:\text{BuPyCl}$ containing $\text{Ru}(\text{bpy})_3^{2+}$ with oxygen. Although it was possible to oxidize these solutions (in sealed tubes) over the melt compositions of $1.2:1$ to $1.9:1$ by oxygen, the time needed to convert $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^{3+}$ (i.e., change of color from orange to green) was longer as the acidity decreased. The green solutions of $\text{Ru}(\text{bpy})_3^{3+}$ was found to be stable for months.

c. AN ALUMINUM-OXYGEN CELL

In view of the observed oxidation of the polypyridine complexes of $\text{Fe}(\text{II})$ and $\text{Ru}(\text{II})$ by oxygen in acidic melts, an attempt was made to see if a cell using oxygen as an oxidant could be made. The reduction of O_2 by $\text{Ru}(\text{bpy})_3^{2+}$ is potentially a useful reaction for batteries since $\text{Ru}(\text{bpy})_3^{3+}$ is a strong and facile oxidizing agent. We have made a preliminary investigation (23) of this possibility by constructing the cell shown in Figure 6. Aluminum oxidation occurs at the anode and $\text{Ru}(\text{bpy})_3^{3+}$ reduction occurs at the cathode. The $\text{Ru}(\text{bpy})_3^{3+}$ is regenerated in the acid melt by oxygen and so $\text{Ru}(\text{bpy})_3^{2+}$ acts as a mediator for O_2 reduction at the

cathode. Thus the net cell reactions are Al oxidation and O_2 reduction; the product of O_2 reduction in the melt is not known at present, but is probably $AlOCl_2^-$. Reduction of $Ru(bpy)_3^{3+}$ by aluminum is extremely slow so no separator was necessary. The cell of Figure 6 gave an open circuit potential of ~ 1.4 V and passed a charge corresponding to 400 turnovers of the ruthenium complex with no significant deterioration. The potential is that which is expected based on the $Ru(bpy)_3^{+3/+2}$ voltammogram (see Figure 1C). The current was limited by mass transport of $Ru(bpy)_3^{3+}$ to the cathode.

2. SPECTROSCOPY

UV-visible absorption spectra for both the bivalent and the trivalent complexes of tris-bipyridine complexes of iron and ruthenium and tris-phenanthrolineiron in the neutral or acidic $AlCl_3:BuPyCl$ melts are shown in Figures 7-9. The trivalent compounds were obtained by the chemical oxidation of the respective divalent complexes in acid melts either by bubbling with oxygen or by trace of O_2 impurity present in the dry box atmosphere. The spectrum of $Ru(bpy)_3^{2+}$ did not change as the melt composition varied from basic to acidic. Thus $Ru(bpy)_3^{2+}$, unlike $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ complexes, does not decompose in the basic melt. The spectra of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ in the neutral melt are identical to their respective spectrum in the slightly acidic melt. In Table 4 the molar absorptivities and maxima wavelengths obtained in this work are summarized and compared with those reported in other solvents (24-31). There is good agreement between positions of the absorption maxima determined here and those from the literature. The intense bands in the visible regions of these compounds are due to the transfer of electronic charge between the d-orbital of the metal ion and the

π -orbitals of the ligand. For the bivalent complexes charge transfer takes place from the metal to the ligand i.e., $t_{2g} \rightarrow \pi^*$ (MLCT) (24,25,30). In the case of trivalent complexes the charge transfer is from the ligand to the metal i.e., $\pi \rightarrow t_{2g}$ (LMCT) (27,31). In addition to these bands, there are other bands in the shorter wavelength portions of all spectra, which because of their higher intensities are outside the spectrum range. Due to the melt UV cutoff at ~ 280 nm, the UV absorption bands of these compounds could not be recorded.

DISCUSSION

Spectroscopic and electrochemical results show that all the complexes studied here are stable (i.e., have fixed coordination spheres) in the melt compositions of 1.0:1.0 to 2:1 $\text{AlCl}_3\text{:BuPyCl}$. Although $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ decompose in the basic melts to form FeCl_4^- , $\text{Ru}(\text{bpy})_3^{2+}$ is stable and does not dissociate, perhaps due to the significantly greater lability of the $\text{Fe}(\text{II})$ -tris complexes over that of ruthenium.

Based on the foregoing observations and results presented in Tables 1-3, we conclude that in the entire region from neutral to 2:1 melts the oxidation of $\text{Fe}(\text{bpy})_3^{2+}$, $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ corresponds to a Nernstian one-electron electrochemically reversible process. Reversible behavior for these couples has been found in other solvents (8,12,13). Consideration of E_f or $E_{1/2}$ from Tables 1-3 indicates that although these values shift slightly toward more positive potentials with increasing melt acidity, the variation in E_f or $E_{1/2}$ in going from 1:1 to 1.9:1 mole ratio for all of these redox couples is less than 90 mV (the reproducibility of $\text{Al}/\text{Al}(\text{III})$ reference electrode is ± 10 mV). This indicates that the influence of variation in the melt composition on the redox properties of these polypyridine complexes is relatively small, but not as small as for ferrocene/ferricinium couple. Robinson and Osteryoung reported that the formal potential value of ferrocene/ferricinium in $\text{AlCl}_3\text{:BuPyCl}$ melts was independent of melt acidity (with the E_f value of 0.27 V vs. $\text{Al}/\text{Al}(\text{III})$) (1). This is understandable since the compact "sandwich" structure of ferrocene/ferricinium compared to the open structure of polypyridine complexes should prevent the close

approach of the solvent molecules to the metal redox center. A possible explanation of the observed variation in E_f for the polypyridine complexes with the melt acidity is the formation of ion-pairs, most probably with $AlCl_4^-$. As the acidity of the melt increases the concentration of $AlCl_4^-$ decreases and E_f becomes more positive. In other words with increasing acidity of the melt the extent of ion-pairing between the polypyridine complexes of iron and ruthenium with $AlCl_4^-$ decreases and the overall positive charge of the complex increases making it more difficult to oxidize.

Comparison of the E_f values for $Fe(bpy)_3^{2+/3+}$, $Fe(phen)_3^{2+/3+}$ and $Ru(bpy)_3^{2+/3+}$ (quoted vs. ferrocene/ferricinium) in different solvents with those in the neutral melt is shown in Table 5. It is obvious from this Table that indeed the redox properties of these couples are relatively insensitive to the nature of the solvent. This is expected since the polypyridine ligand should somewhat shield the solvent from the metal cation. Although the redox properties of these polypyridine couples appear to be largely independent of the solvent, indicating that they might be used as internal reference redox couples, they apparently do not offer any advantage over the ferrocene, particularly in $AlCl_3:BuPyCl$ melts.

In Table 6 values of diffusion coefficients for the polypyridine complexes of iron and ruthenium are given. The values of D were obtained from RDE experiments using the Levich equation:

$$I_l = 0.62 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C_0 \quad (3)$$

where I_l is the limiting current in amperes, n the number of electrons transferred, F the Faraday constant, A the area of the electrode in cm^2 ,

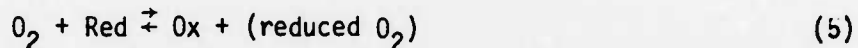
ω the rotation rate in radians/sec, ν the kinematic viscosity and C_0 the concentration of the electroactive species in mol/cm^3 (18). Diffusion coefficient for $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Fe}(\text{phen})_3^{2+}$ were only determined in the neutral melt where there was no chemical oxidation of the $\text{Fe}(\text{II})$ complex and its concentration was known accurately. The observed change in the D value for $\text{Ru}(\text{bpy})_3^{2+}$ in Table 6 can be attributed to changes in the viscosity (η) of the melt. The values of D and η are related by the modified Stokes-Einstein equation (33):

$$D = \frac{\kappa T}{4\pi\eta r} \quad (4)$$

where κ is the Boltzman constant and r is the radius of the diffusing species. The ηD values for $\text{Ru}(\text{bpy})_3^{2+}$ (tabulated in Table 6) are constant throughout the entire range of melt compositions studied here. Values of r calculated from equation (4) for polypyridine complexes are also listed in Table 6. These radii are in reasonable agreement with their corresponding crystallographic values (34,35), indicating that solvation is not very important in this medium for these compounds.

Although the "spontaneous" oxidation of some aromatic hydrocarbons (with $E_{1/2}$ of less than ~ 1.4 V) in highly acidic $\text{AlCl}_3:\text{BuPyCl}$ melts has been observed by Robinson and Osteryoung, the nature of the oxidizing species was not speculated upon (1). It is clear from this work that oxygen is an oxidant which oxidizes species with the $E_{1/2}$ of ~ 1.3 V and less in acidic $\text{AlCl}_3:\text{BuPyCl}$ melts. Considering our results and those observed previously for oxidations of aromatic hydrocarbons (1) and iodide (6), we conclude that O_2 can oxidize any species with an $E_{1/2}$ of 1.4 V or less in the acidic melts regardless of its chemical nature. In other words the oxidation process is insensitive to the nature of the

reductant and only depends on its formal potential, presumably according to the following reaction:



with $E_f \text{ O}_2/(\text{reduced O}_2) > E_f \text{ Red/Ox}$

Since neither the reduction of oxygen nor electrochemistry from its reduction product can be seen, it is not known whether the decrease in the rate of oxidation with decreasing melt acidity results from slow kinetics or unfavorable thermodynamics. One possible explanation is that by decreasing melt acidity, the value of E_f for $\text{O}_2/(\text{reduced O}_2)$ shifts to negative potentials. Indeed the absence of chemical oxidation of these compounds in the neutral or basic melts is a good indication of such an explanation. The other possibility is that the solubility of O_2 decreases drastically as the acidity decreases, making the oxidation more difficult.

It should also be pointed out that O_2 impurity in the dry-box may not be the sole trace oxidant present in these melts. Perchlorate, as indicated above, also functions as an oxidant in acidic melts. Recent work on the reduction of proton arising from the addition of water to the melt indicates that the potential for evolution of hydrogen moves in the positive direction with increasing melt acidity, suggesting that the "proton", which may arise from HCl or an $-\text{Al}-\text{O}-\text{H}$ entity formed as a result of water addition, is a stronger oxidant in acidic than basic melts (36). However, experiments at a platinum electrode in a melt containing both water and the Ru-complex indicated that the ruthenium reduction takes place at more positive potentials than does hydrogen evolution. Nevertheless, the ability of proton to act as an oxidant in these melts at the trace levels should not be overlooked.

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CREDIT

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Table 1 Summary of Voltammetric Parameters for $\text{Fe}(\text{bpy})_3^{2+/3+}$ in AlCl_3 : BuPyCl Melts.^a

| Melt Composition | Scan Rate(v) mV/s | Cyclic Voltammetric Data | | | | | RDE Data | | |
|---------------------|----------------------|--------------------------|---------------|-------------|--------------------|---------------|--|----------------------|-----------------|
| | | E_p^c mV | E_a^d mV | E_f mV | ΔE_p mV | i_p^a/i_p^c | $i_p^a/\sqrt{v}^{1/2}$ mA cm ⁻² v ^{-1/2} s ^{1/2} | Rotation Rate rpm | $E_{1/2}$ mV |
| 1:1 | 10 | 927 | 992 | 960 | 65 | 1.00 | 0.507 | 600 | 957 |
| | 20 | 927 | 992 | 960 | 65 | 1.01 | 0.510 | 900 | 959 |
| | 50 | 922 | 996 | 959 | 74 | 1.01 | 0.514 | 1600 | 960 |
| | 100 | 920 | 998 | 959 | 78 | 1.00 | 0.515 | 2000 | 959 |
| | | | | | | | | 2500 | 963 |
| 1.05:1 | 10 | 935 | 1000 | 968 | 65 | 1.01 | 0.413 | 400 | 965 |
| | 20 | 935 | 1000 | 968 | 65 | 1.02 | 0.420 | 600 | 965 |
| | 50 | 936 | 1002 | 969 | 66 | 1.01 | 0.428 | 900 | 967 |
| | 100 | 931 | 1005 | 968 | 74 | 1.00 | 0.430 | 1600 | 970 |
| | 200 | 930 | 1010 | 970 | 80 | 1.00 | 0.433 | 2000 | 972 |
| 1.2:1 | 10 | 950 | 1015 | 982 | 65 | 1.01 | 0.451 | 600 | 980 |
| | 20 | 950 | 1015 | 982 | 65 | 1.01 | 0.478 | | |
| | 50 | 948 | 1015 | 981 | 67 | 1.00 | 0.480 | | |
| | 100 | 945 | 1020 | 982 | 75 | 1.01 | 0.494 | | |
| | | | | | | | | | |
| 1.4:1 | 10 | 963 | 1025 | 994 | 62 | 1.01 | 0.407 | 600 | 990 |
| | 20 | 963 | 1025 | 994 | 62 | 1.00 | 0.412 | | |
| | 50 | 960 | 1028 | 994 | 68 | 0.99 | 0.414 | | |
| | 100 | 960 | 1030 | 995 | 70 | 1.02 | 0.414 | | |
| | | | | | | | | | |
| 1.7:1 | 10 | 990 | 1055 | 1022 | 65 | 1.02 | 0.385 | 600 | 1020 |
| | 20 | 990 | 1055 | 1022 | 65 | 1.04 | 0.389 | | |
| | 50 | 990 | 1057 | 1023 | 67 | 1.01 | 0.379 | | |
| | 100 | 985 | 1060 | 1022 | 75 | 1.00 | 0.383 | | |
| | | | | | | | | | |
| 1.9:1 | 10 | 1007 | 1073 | 1040 | 66 | 0.98 | 0.363 | 600 | 1038 |
| | 20 | 1007 | 1073 | 1040 | 66 | 0.99 | 0.358 | | |
| | 50 | 1007 | 1075 | 1041 | 68 | 1.00 | 0.364 | | |
| | 100 | 1005 | 1075 | 1040 | 70 | 0.99 | 0.369 | | |
| | | | | | | | | | |

a. All potentials are in mV vs. $\text{Al}/\text{Al}(\text{III})$ in 2:1 AlCl_3 : BuPyCl, at $T=40^\circ\text{C}$.

b. Mole ratio of AlCl_3 : BuPyCl.

Table 2 Summary of Voltammetric Parameters for Fe(phen)₃^{2+/3+} in AlCl₃: BuPyCl Melts.^a

| Melt Composition | Scan Rate (°) mV/s | Cyclic Voltammetric Data | | | | | RDE Data | | |
|------------------|--------------------|--------------------------------|--------------------------------|-------------------|--------------------|--|--|-------------------|---------------------|
| | | E _p ^c mV | E _a ^p mV | E _f mV | ΔE _p mV | i _p ^a /i _p ^c | i _a ^a /i _p ^c 1/2 | Rotation Rate rpm | E _{1/2} mV |
| 1:1 | 10 | 965 | 1033 | 999 | 68 | 1.00 | 0.242 | 600 | 1002 |
| | 20 | 965 | 1035 | 1000 | 70 | 1.02 | 0.230 | 900 | 1005 |
| | 50 | 965 | 1035 | 1000 | 70 | 1.01 | 0.226 | 1600 | 1007 |
| | 100 | 962 | 1040 | 1001 | 78 | 1.01 | 0.233 | 2000 | 1005 |
| 1.05:1 | 10 | 976 | 1040 | 1008 | 64 | 1.02 | 0.268 | 600 | 1008 |
| | 20 | 975 | 1042 | 1008 | 67 | 1.00 | 0.288 | 900 | 1008 |
| | 50 | 973 | 1045 | 1009 | 72 | 1.01 | 0.293 | 1600 | 1007 |
| | 100 | 973 | 1047 | 1010 | 74 | 1.01 | 0.293 | 2500 | 1007 |
| 1.2:1 | 10 | 990 | 1052 | 1021 | 62 | 1.03 | 0.341 | 600 | 1020 |
| | 20 | 990 | 1055 | 1022 | 65 | 1.02 | 0.343 | 900 | 1021 |
| | 50 | 990 | 1058 | 1024 | 68 | 1.01 | 0.335 | 1600 | 1022 |
| | 100 | 988 | 1060 | 1024 | 72 | 1.00 | 0.338 | 2000 | 1025 |
| 1.4:1 | 10 | 1007 | 1070 | 1038 | 63 | 1.02 | 0.319 | 600 | 1038 |
| | 20 | 1007 | 1070 | 1038 | 63 | 1.02 | 0.323 | 900 | 1040 |
| | 50 | 1005 | 1072 | 1038 | 67 | 1.01 | 0.320 | 1600 | 1038 |
| | 100 | 1000 | 1075 | 1037 | 75 | 1.00 | 0.314 | 2000 | 1040 |
| 1.7:1 | 10 | 1035 | 1100 | 1067 | 65 | 1.01 | 0.270 | 600 | 1065 |
| | 20 | 1035 | 1100 | 1067 | 65 | 1.01 | 0.276 | 900 | 1065 |
| | 50 | 1032 | 1102 | 1067 | 70 | 1.00 | 0.280 | 1600 | 1065 |
| | 100 | 1032 | 1105 | 1068 | 73 | 1.00 | 0.275 | 2000 | 1065 |
| 1.9:1 | 10 | 1052 | 1118 | 1085 | 66 | 1.00 | 0.264 | 600 | 1083 |
| | 20 | 1052 | 1120 | 1086 | 68 | 1.01 | 0.261 | 900 | 1083 |
| | 50 | 1050 | 1120 | 1085 | 70 | 0.98 | 0.261 | 1600 | 1083 |
| | 100 | 1050 | 1120 | 1085 | 70 | 0.98 | 0.260 | 2000 | 1083 |

a. All potentials are in mV vs. Al/Al(III) in 2:1 AlCl₃: BuPyCl, at T=40°C.

b. Mole ratio of AlCl₃: BuPyCl

Table 3 Summary of Voltammetric Parameters for Ru(bpy)₃^{2+/3+} in AlCl₃: BuPyCl Melts.^a

| Melt Composition | b | Scan Rate(ν) mV/s | Cyclic Voltammetric Data | | | | | | RDE Data | |
|---------------------|---|----------------------------|--------------------------|---------------|-------------|--------------------|---------------|---|----------------------|-----------------|
| | | | E_p^c mV | E_p^a mV | E_f mV | ΔE_p mV | i_p^a/i_p^c | $i_p^a/\nu^{1/2}$ mA cm ⁻² V ^{-1/2} s ^{1/2} | Rotation Rate rpm | $E_{1/2}$ mV |
| 1:1 | | 10 | 1130 | 1198 | 1164 | 68 | 1.00 | 0.308 | 600 | 1163 |
| | | 20 | 1130 | 1198 | 1164 | 68 | 1.03 | 0.300 | 900 | 1163 |
| | | 50 | 1127 | 1202 | 1165 | 75 | 1.02 | 0.329 | 1600 | 1163 |
| | | 100 | 1127 | 1204 | 1165 | 77 | 1.01 | 0.327 | 2000 | 1163 |
| 1.05:1 | | 10 | 1140 | 1204 | 1172 | 64 | 1.00 | 0.357 | 400 | 1170 |
| | | 20 | 1140 | 1204 | 1172 | 64 | 1.02 | 0.360 | 600 | 1170 |
| | | 50 | 1138 | 1206 | 1172 | 68 | 1.03 | 0.364 | 900 | 1170 |
| | | 100 | 1138 | 1208 | 1173 | 70 | 1.03 | 0.359 | 1600 | 1170 |
| 1.2:1 | | 200 | 1136 | 1210 | 1173 | 74 | 1.03 | 0.353 | 2000 | 1170 |
| | | | | | | | | | 2500 | 1172 |
| | | | | | | | | | 3600 | 1175 |
| | | | | | | | | | 600 | 1183 |
| 1.4:1 | | 10 | 1152 | 1216 | 1184 | 64 | 1.04 | 0.331 | | |
| | | 20 | 1152 | 1216 | 1184 | 64 | 1.06 | 0.329 | | |
| | | 50 | 1150 | 1218 | 1184 | 68 | 1.05 | 0.322 | | |
| | | 100 | 1150 | 1220 | 1185 | 70 | 1.05 | 0.321 | | |
| 1.7:1 | | 10 | 1170 | 1234 | 1202 | 64 | 1.02 | 0.344 | 600 | 1202 |
| | | 20 | 1170 | 1234 | 1202 | 64 | 1.03 | 0.352 | | |
| | | 50 | 1170 | 1236 | 1204 | 68 | 1.03 | 0.343 | | |
| | | 100 | 1168 | 1240 | 1204 | 72 | 1.04 | 0.339 | | |
| 1.9:1 | | 10 | 1198 | 1262 | 1230 | 64 | 1.02 | 0.332 | 600 | 1230 |
| | | 20 | 1198 | 1262 | 1230 | 64 | 1.03 | 0.338 | | |
| | | 50 | 1195 | 1265 | 1230 | 70 | 1.02 | 0.339 | | |
| | | 100 | 1195 | 1265 | 1230 | 70 | 1.04 | 0.340 | | |
| 1.9:1 | | 10 | 1220 | 1284 | 1252 | 64 | 1.02 | 0.331 | 600 | 1255 |
| | | 20 | 1220 | 1284 | 1252 | 64 | 1.01 | 0.333 | | |
| | | 50 | 1220 | 1288 | 1254 | 68 | 1.02 | 0.325 | | |
| | | 100 | 1222 | 1290 | 1256 | 68 | 1.03 | 0.327 | | |

a. All potentials are in mV vs. Al/Al(III) in 2:1 AlCl₃: BuPyCl, at T= 40° C

b. Mole ratio of AlCl₃: BuPyCl

Table 4. Spectroscopic Data for Polypyridine Complexes Of Ru and Fe in
 $\text{AlCl}_3\text{:BuPyCl}$ Melts.^a

| Complex | color | λ_{max} , nm | molar abs. $\text{M}^{-1} \text{cm}^{-1}$ | Values from the Literature |
|---------------------------------|---------------|--------------------------------|--|---|
| | | | | λ_{max} , nm (molar abs., $\text{M}^{-1} \text{cm}^{-1}$) |
| $\text{Ru}(\text{bpy})_3^{2+}$ | orange | 454 | 14,000 | 453(13800) ^c , 450(14000) ^d |
| $\text{Ru}(\text{bpy})_3^{3+}$ | green | 424 | 3200 | 418(~3000) ^c |
| $\text{Fe}(\text{bpy})_3^{2+}$ | red | 523 | 8700 | 522(8740) ^e , 520(8240) ^f |
| $\text{Fe}(\text{bpy})_3^{3+}$ | greenish-blue | 627 | 380 | 618(284) ^g , 613(289) ^h |
| $\text{Fe}(\text{phen})_3^{2+}$ | red | 512 | 10,800 | 510(11300) ⁱ , 510(11100) ^j |
| $\text{Fe}(\text{phen})_3^{3+}$ | blue | ~610 | 800 | 590(600) ^j , 602(870) ^k |

a. these spectra were obtained either in the neutral or acidic melts (see text for details)
b. molar absorptivities are accurate to $\pm 5\%$.

- c. reference 24
- d. reference 25
- e. reference 26
- f. reference 27
- g. reference 13
- h. reference 28
- i. reference 29
- j. reference 30
- k. reference 31

Table 5. Formal Potentials for Polypyridine Complexes of Ru(II)/(III) and Fe(II)/(III) in Various Solvents vs. Ferrocene/Ferricinium Couple.

| Solvent | E_f^a | | |
|-------------------------------|-----------------------------|----------------------------|----------------------------|
| | $\text{Fe(phen)}_3^{2+/3+}$ | $\text{Fe(bpy)}_3^{2+/3+}$ | $\text{Ru(bpy)}_3^{2+/3+}$ |
| Water | 743 ^b | 718 ^b | 921 ^b |
| Acetonitrile | 686 ^c | 670 ^d | 900 ^e |
| 1:1 AlCl ₃ :BuPyCl | 730 ^f | 690 ^f | 894 ^f |
| Nitromethane | 721 ^c | 727 ^d | |

a. Formal potential for each redox couple is quoted in mV vs. E_f for Ferrocene/Ferricinium couple in same solvent i.e., $E_f = E_f(\text{redox couple}) - E_f(\text{Ferrocene/Ferricinium})$

b. Reference 17

c. Reference 12

d. Reference 16

e. Reference 37

f. This work

Table 6. Diffusion Coefficients (at $T = 40^\circ \text{C}$) and Radii of Polypyridine
Fe(II) and Ru(II) Complexes in $\text{AlCl}_3\text{:BuPyCl}$ Melts.^a

| Melt Composition | $\text{Ru}(\text{bpy})_3^{2+}$ | | $\text{Fe}(\text{bpy})_3^{2+}$ | $\text{Fe}(\text{phen})_3^{2+}$ |
|---|---|---|---|---|
| | $D \times 10^7$ cm^2/s | $D \eta 10^8$ $\text{g cm}^2/\text{s}^2$ | $D \times 10^7$ cm^2/s | $D \times 10^7$ cm^2/s |
| 1:1 | 2.75 | 6.05 | 2.61 | 2.43 |
| 1.05:1 | 2.88 | 6.06 | | |
| 1.2:1 | 2.99 | 6.00 | | |
| 1.4:1 | 3.35 | 6.04 | | |
| 1.7:1 | 3.67 | 6.05 | | |
| 1.9:1 | 4.07 | 6.11 | | |
| Average = 6.04 0.04 | | | | |
| calculated radius of the complex, nm | 0.57 | | 0.60 | 0.64 |

a. Values of the viscosity (η) and density used in the calculation of D , $D\eta$ and radius are taken from reference 20.

FIGURE CAPTIONS

- Figure 1. Cyclic voltammograms in 1.05:1 $\text{AlCl}_3\text{:BuPyCl}$ melts. Scan rate = 50 mV/s; $T = 40^\circ\text{C}$. (a) 3.2 mM $\text{Fe}(\text{bpy})_3^{2+}$, GC electrode with $A = 0.454 \text{ cm}^2$. (b) 1.8 mM $\text{Fe}(\text{phen})_3^{2+}$, GC electrode with $A = 0.454 \text{ cm}^2$. (c) 2.8 mM $\text{Ru}(\text{bpy})_3^{2+}$, GC with $A = 0.196 \text{ cm}^2$.
- Figure 2. Plots of current at various potentials vs. $\omega^{1/2}$ for the oxidation of $\text{Fe}(\text{bpy})_3^{2+}$ (dashed lines), and $\text{Fe}(\text{phen})_3^{2+}$ (solid lines) in 1.0:1.0 $\text{AlCl}_3\text{:BuPyCl}$. E in mV: (1) 1000, (2) 1050, (3) 1300.
- Figure 3. Plots of E vs. $\log \frac{I_1 - I}{I}$ for the oxidation of (1) $\text{Fe}(\text{bpy})_3^{2+}$, (2) $\text{Fe}(\text{phen})_3^{2+}$, (3) $\text{Ru}(\text{bpy})_3^{2+}$ in 1.05:1 $\text{AlCl}_3\text{:BuPyCl}$.
- Figure 4. RDE voltammograms for a 1.2:1 $\text{AlCl}_3\text{:BuPyCl}$ melt with initial concentration of 3.8 mM $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$, recorded as a function of time. Scan rate = 5 mV/s; rotation rate = 600 rpm; $T = 40^\circ\text{C}$; GC electrode with $A = 0.454 \text{ cm}^2$. Time in minutes: (1) 0, (2) 35, (3) 65, (4) 110, (5) 300.
- Figure 5. Voltammograms for 3.1 mM $\text{Fe}(\text{bpy})_3(\text{ClO}_4)_2$ dissolved in a 0.95:1 $\text{AlCl}_3\text{:BuPyCl}$ melt (which actually corresponds to 3.1 mM FeCl_4^{2-} , see text). $T = 40^\circ\text{C}$; GC electrode with $A = 0.454 \text{ cm}^2$. (a) Cyclic voltammogram with scan rate = 100 mV/s. (b) RDE voltammogram with scan rate = 5 mV/s and rotation rate = 600 rpm.
- Figure 6. An Aluminum-Oxygen cell configuration.
- Figure 7. Absorption spectra of a 1.05:1 $\text{AlCl}_3\text{:BuPyCl}$ (dashed line) and 0.96 mM $\text{Ru}(\text{bpy})_3^{2+}$ in 1.05:1 $\text{AlCl}_3\text{:BuPyCl}$ melt (solid line). Cell thickness = 0.1 cm.
- Figure 8. Absorption spectra of: 1.17 mM $\text{Fe}(\text{bpy})_3^{2+}$ in 1:1 melt, cell thickness = 0.1 cm (---); 2.5 mM $\text{Fe}(\text{phen})_3^{3+}$ in 1.9:1 melt, cell thickness = 1 cm (—).

Figure 9. Absorption spectra of: 1.45 mM $\text{Fe}(\text{phen})_3^{2+}$ in 1:1 melt, cell thickness = 0.1 cm (---); 1.7 mM $\text{Ru}(\text{bpy})_3^{3+}$ in 1.9:1 melt, cell thickness = 0.1 cm (-.-); 3.87 mM $\text{Fe}(\text{bpy})_3^{3+}$ in 1.2:1 melt, cell thickness = 1 cm (—).

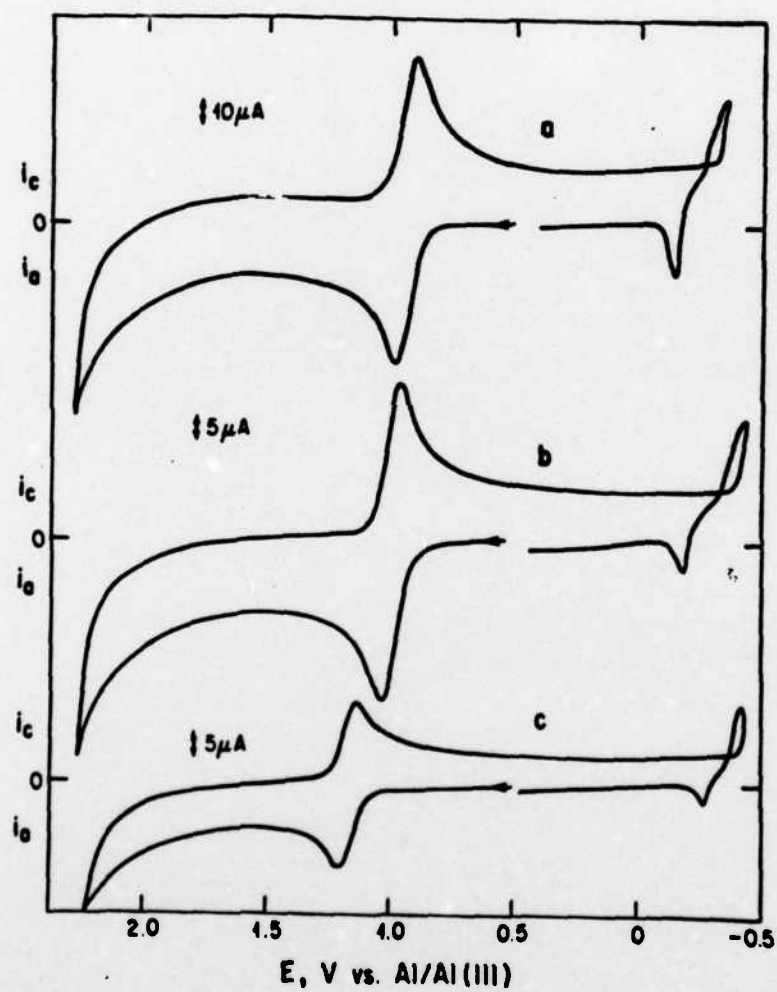


FIGURE 1

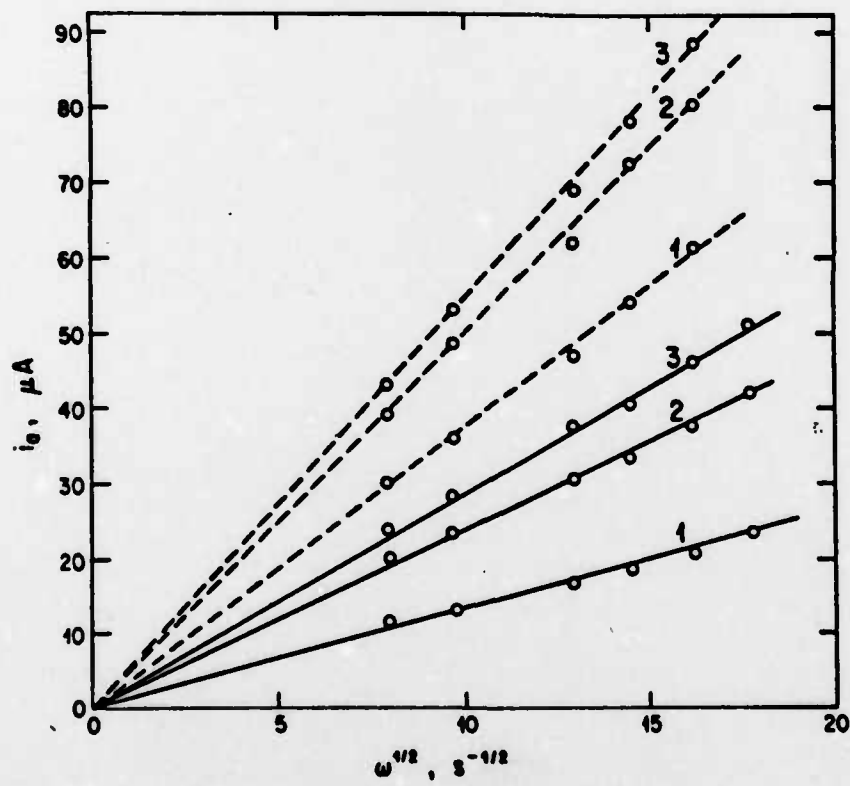


FIGURE 2

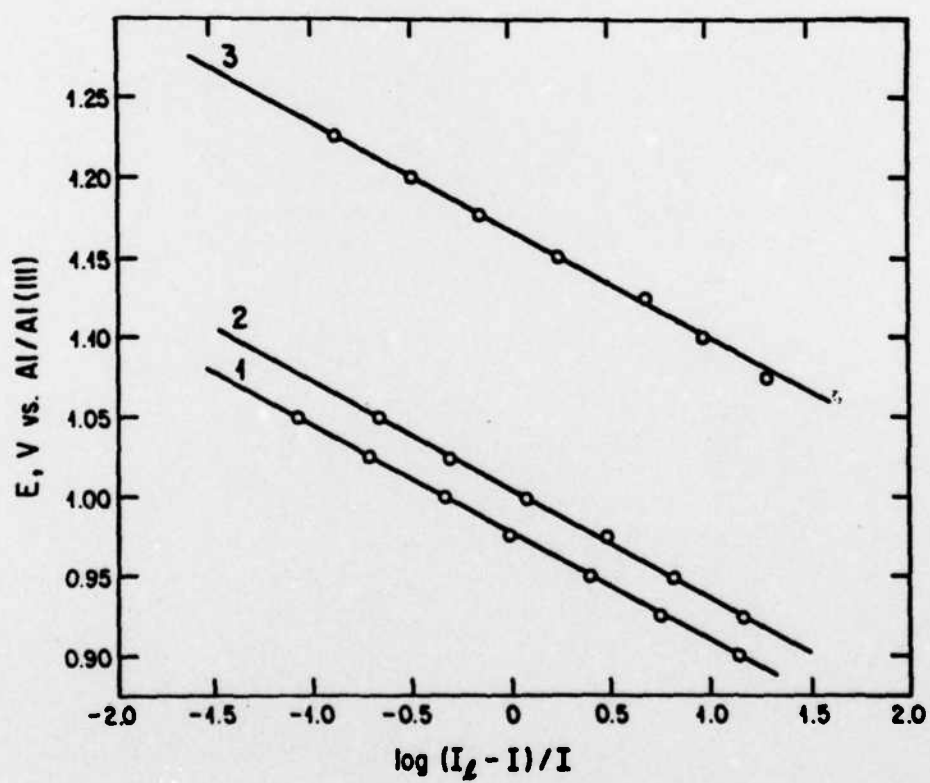


FIGURE 3

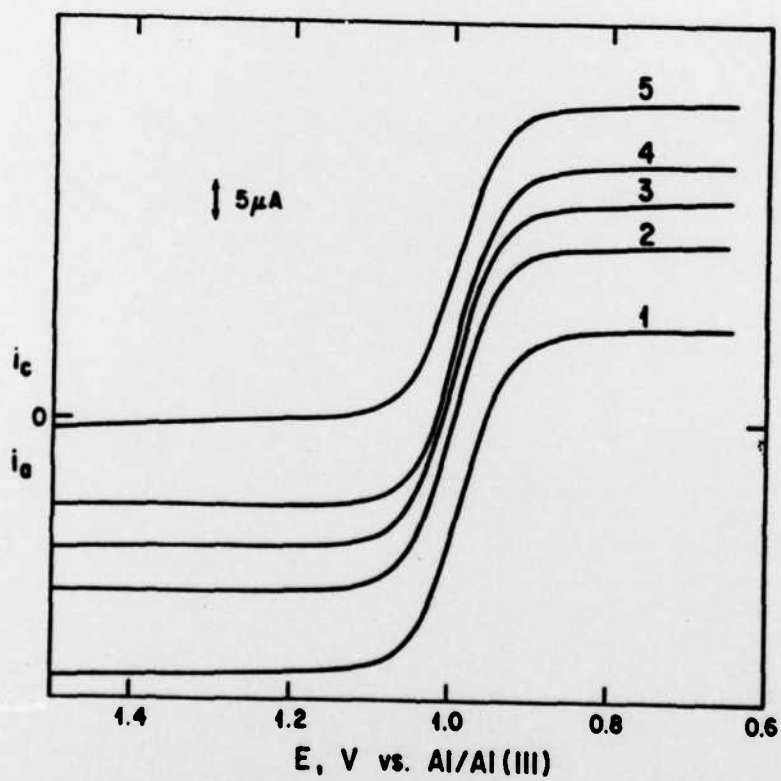


FIGURE 4

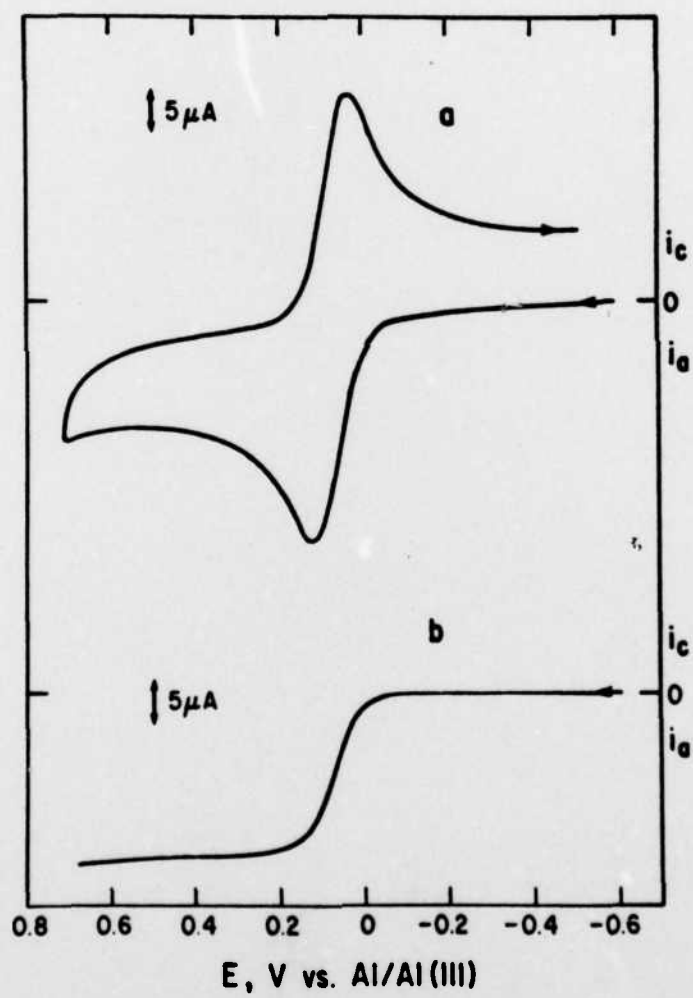


FIGURE 5

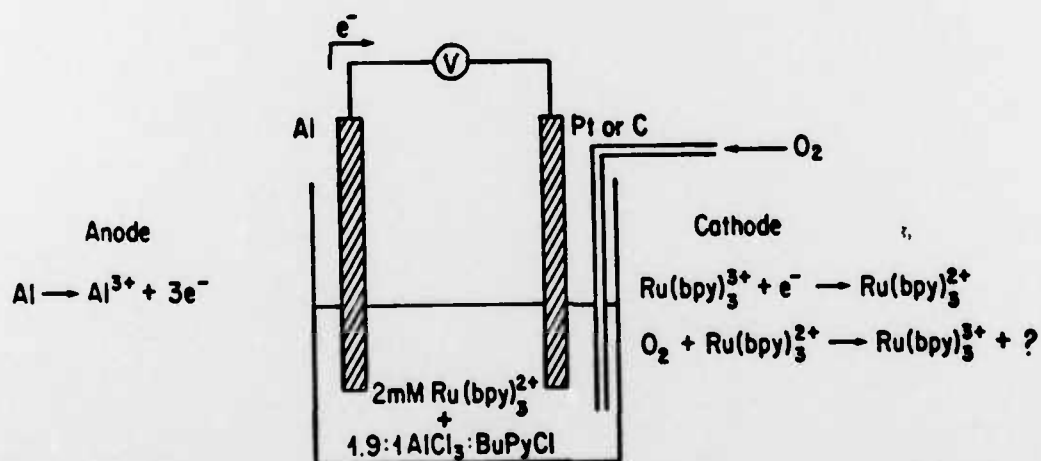


FIGURE 6

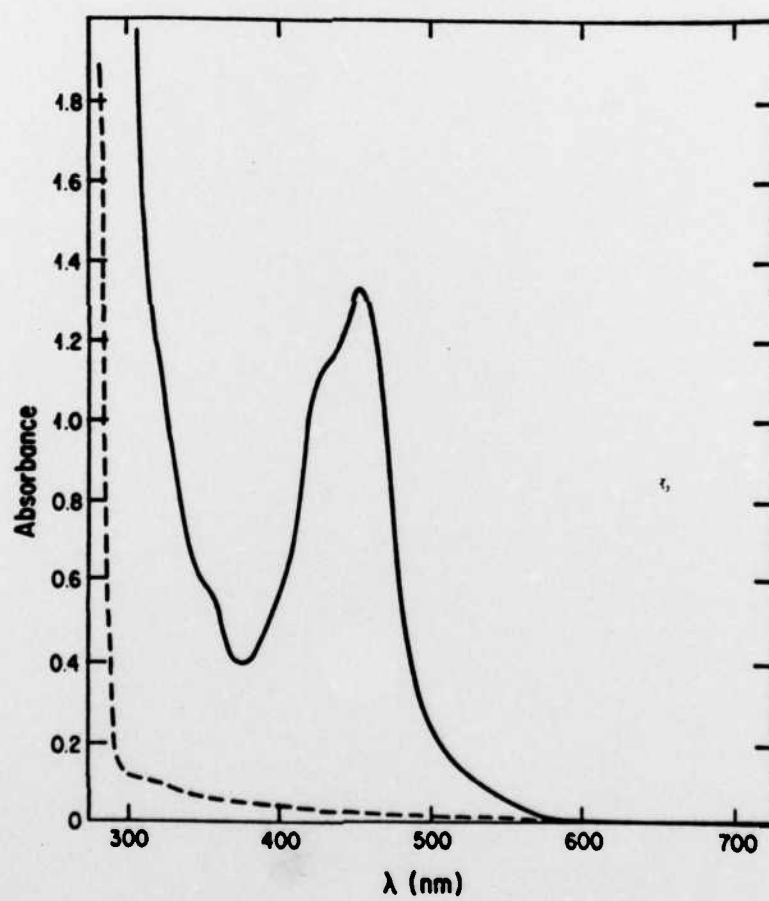


FIGURE 7

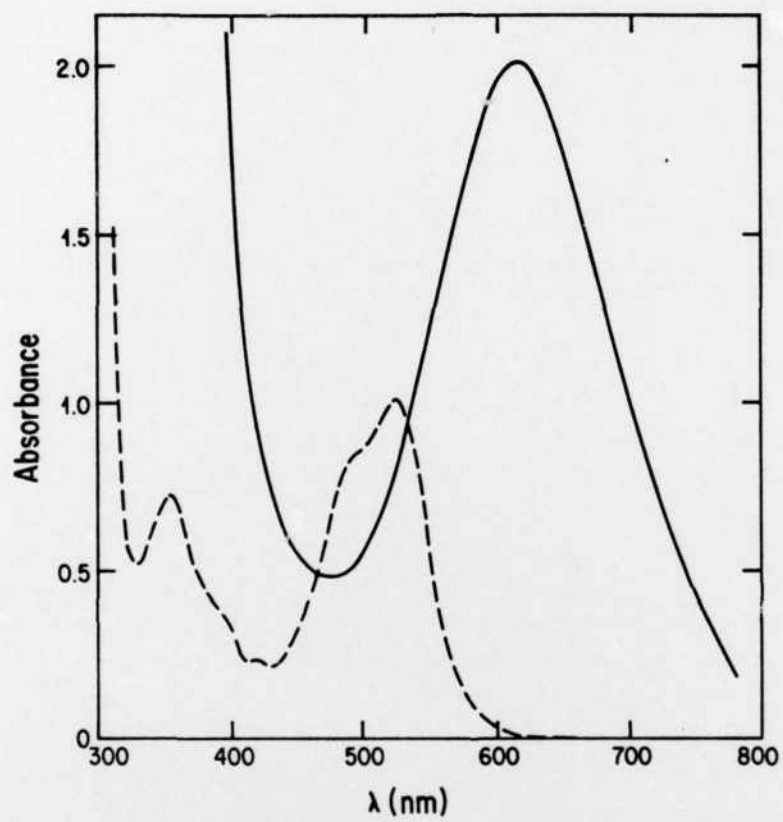


FIGURE 8

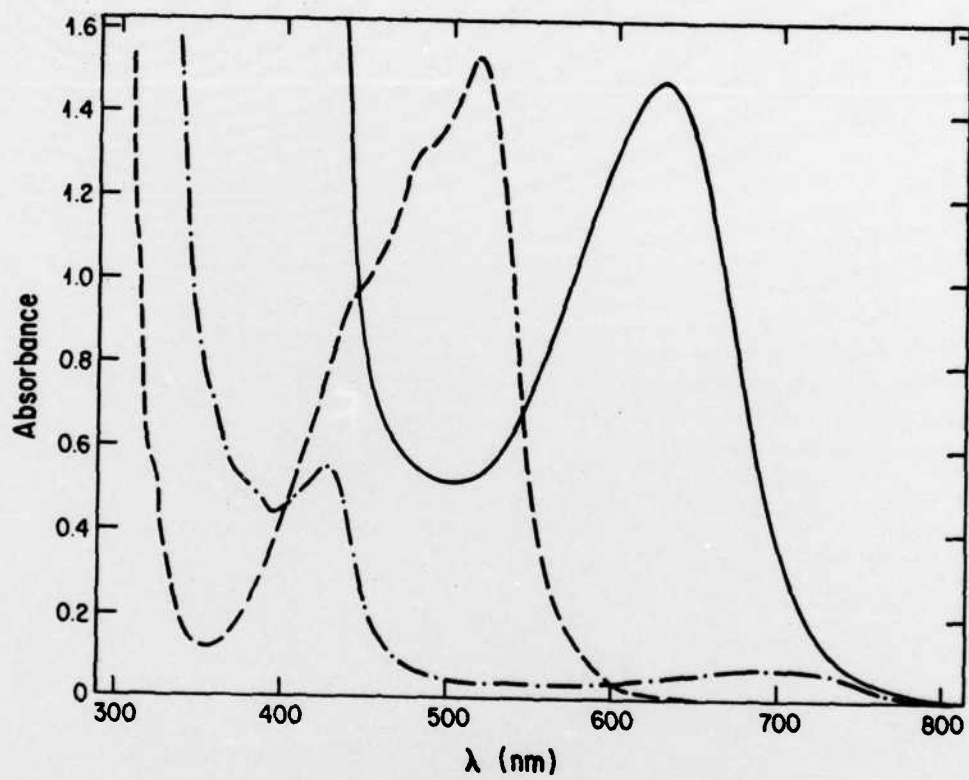


FIGURE 9

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